DEVELOPMENT OF THE MODIFIED ZEOLITE-A CATALYST FOR THE DIRECT CONVERSION OF METHANE TO LIQUID HYDROCARBONS

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I declared that this thesis entitled

'Development of the modified Zeolite-A catalyst for the direct conversion of methane to liquid hydrocarbons' is the result of my own research except as cited in the references. The thesis has not been accepted for any degree is not concurrently submitted candidature of any degree.

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Date : 9 MAY 2008

Special dedicated to my beloved mother and father

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In the name of Allah the Most Gracious and Most Merciful

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ABSTRACT

The characteristic of Zeolite-A loaded with iron and zinc on the direct conversion of methane to liquid hydrocarbons is investigated. Zeolite-A is loaded with different mass ratio of zinc and iron. Thermo Gravimetric Analysis (TGA), X-Ray Diffraction (XRD), and Fourier transform spectroscopy (FTIR) are used to analyze the physicochemical properties of the modified zeolite such as functional group, surface area and average diameter of unit cell. The absence of the iron content in the catalyst does not affect the framework and the crystalline of the catalyst but only affect the size of the unit cell and the surface area of the catalyst. As compare to zinc, it has modified the crystalline and framework of the catalyst. The result indicated that Zeolite-A with 8% of zinc and 2% of iron of metal doped is the most suitable catalyst for the methane conversion to liquid hydrocarbons. The catalyst has high thermal stability, high surface area, and high average diameter of unit cell and has low weight loss.

ABSTRAK

Kajian ciri-ciri Zeolite-A dengan campuran logam besi dan zink terhadap proses penukaran metana secara terus kepada hidrokarbon cecair telah dijalankan. Zeolite-A akan dicampur dengan nisbah jisim zinc dan iron yang berbeza-beza. Thermo Gravimetric Analysis (TGA), X-Ray Diffraction (XRD), dan Fourier transform spectroscopy (FTIR) akan digunakan untuk mengesan fizikal kimia pemangkin yang telah diubahsuai seperti kumpulan berfungsi, luas permukaan dan diameter purata unit cell. Kehadiran unsur besi dalam pemangkin tidak mengubah rangka dan stuktur kristal tetapi hanya mengubah saiz unit sel dan luas permukaan pemangkin tersebut. Berbanding dengan unsur zink, ia mengubah rangka dan struktur kristal pemangkin tersebut. Keputusan menunjukkan bahawa Zeolite-A dengan campuran 8% zink dan 2% besi merupakan pemangkin yang paling sesuai untuk proses penukaran metana secara terus kepada hidrokarbon cecair. Pemangkin ini mempunyai kestabilan termal yang tinggi, permukaan pemangkin yang luas, saiz unit sel yang besar dan mempunyai kadar pengurangan jisim yang rendah.

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TGA	Thermo Gravimetric Analysis
FTIR	Fourier Transform Infrared Spectroscopy
XRD	X-Ray Diffraction

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CHAPTER 1

INTRODUCTION

1.1 Research Background

Natural gas consists of mixture of hydrocarbon gases. The characteristic of the natural gas is colorless, shapeless, and odorless in its pure form. Natural gas is formed primarily of methane but it also includes ethane, propane, butane and pentane. Table 1.1 show outlines the typical makeup of natural gas before it is refined. Natural gas is considered 'dry' when it is almost pure methane, having had most of the other commonly associated hydrocarbons removed. When other hydrocarbons present, the natural gas is 'wet' (Thomas and Dawe, 2003).

Table 1.1 The typical composition of natural gas before it is refined (Kvenvolden, 1995)

Typical Composition of Natural gas		
Methane	CH_4	70-90%
Ethane	C_2H_6	0-20%
Propane	C_3H_8	0-20%
Butane	C_4H_{10}	0-20%
Carbon Dioxide	CO_2	0-8%
Oxygen	O_2	0-0.2%
Nitrogen	N_2	0-5%
Hydrogen Sulphide	H_2S	0-5%
Rare Gases	A, He, Ne, Xe	trace

In the last several decades, methane represents over 90% of the natural gas content and hence it is considered as promising source with high hydrocarbon content (Mat *et. al.,* 1999). However, not all the available and produced methane is utilized. A lot of effort has been considered toward the conversion of methane to value-added products such as transportable liquid hydrocarbons and chemicals. Traditionally, there are two competing demands for natural gas. It is used as a clean fuel in power generation, industrial kilns and furnaces, vehicles, and domestic heating. Natural gas is also demanded as a feedstock for petrochemical and chemical industries (Mat *et. al.,* 1999).

Gas to liquids or GTL is a refinery process to convert natural gas or other gaseous hydrocarbons into longer-chain hydrocarbons (Aguiar *et. al.,* 2005). Methane-rich gases are converted into liquid fuels either via direct conversion or via syngas as an intermediate, using the Fischer Tropsch process (Yagi *et. al.,* 2005). Using such processes, refineries can convert some of their gaseous waste products into valuable fuel oils, which can be sold as or blended only with Diesel fuel (Vosloo, 2001). The process may also be used for the economic extraction of gas deposits in locations where it is not economic to build a pipeline. This process will be increasingly significant as crude oil resources are depleted, while natural gas supplies are projected to last into the 22nd century (Wittcoff *et. al.,* 2004).

The direct conversion of natural gas to liquid hydrocarbons has not yet been successfully economized in an inexpensive process. The conversions of methane to gasoline by direct routes are still at low activity and selectivity (Amin *et al.*, 2006). These processes are possible if the reaction is carried out by controlled oxidation over a suitable catalyst (Mat *et. al.,* 1999). Recent studies have shown that modification of ZSM-5 zeolite by ion exchange, direct synthesis or wet impregnation method with metal oxides of different size and chemical properties are very important to control its acidity and shape selectivity. These modification methods led to an improvement in the catalytic activity and gasoline selectivity. When the acidity is increased by exchanging the zeolite with alkali metal cations, the conversion of methane to hydrocarbons is slightly enhanced. As a result, the metal containing

ZSM-5 can produce higher conversion hydrocarbons in methane oxidation (Amin *et. al.*, 2004).

The performance for direct methane conversion to higher hydrocarbons mainly depends on the physicochemical properties of the catalyst and this process uses zeolite as a catalyst. Physicochemical properties such as surface area and thermal stability are the factors to achieve the higher conversion and quality for this process. Modification by incorporation of elements of different size and different chemical features on zeolite is important to control the acidity and the shape selectivity of a specific zeolite structure.

1.2 Problem Statement

Numerous recent researches have demonstrated the feasibility of direct transformation of methane into products of higher added values such as olefins, aromatics and oxygenous derivatives .These processes are possible if the reaction is carried out by controlled oxidation over a suitable catalyst.

In practice, two routes for direct methane conversions to higher hydrocarbons have been identified. There are oxidative coupling and methane aromatization. A lot of efforts have led to a significant increase in the activity and selectivity of the applied catalyst. Unfortunately, the maximum yield obtained is about 20%, which means that the process is economically unfeasible (Huggil *et. al.,* 2005). In the partial oxidation process, methane reacts with oxygen in the presence of catalyst to produce methanol. Unfortunately, the yield of methanol is too low (below 10%) and beyond industrial interest (Zhang *et. al.,* 2002; Michalkiewicz, 2004, Michalkiewicz, 2006). Direct conversion of methane to mainly ethane and ethene has been observed over fluorinated H-mordenite zeolite at 525^{o}C, but with very poor methane conversion far below 1% (Kowalak *et. al.,* 1988). These low conversions are quite expected due to an unfavorable thermodynamic equilibrium at temperatures below 1000^{o}C.

The application of zeolite for plasma catalytic methane conversion (PCMC) to higher hydrocarbons at very low gas temperature (room temperature to 200oC) by using Zeolites NaY, HY, NaX, NaA, Linde Type 5A and Na-ZSM-5 have been tested (Chang-jun Liu, 1999). NaA showed produce higher methane conversion (49%) compare using Na-ZSM-5 (44.6%) (Chang-jun Liu, 1999).

The present study focuses on the direct conversion of methane to liquid hydrocarbons. In order to overcome the current problems, the Zeolite-A will be doped with iron and zinc with different mass ratio in order to change the structure catalyst, thermal stability and other physicochemical to improve the quality of catalyst.

1.3 Research Objective

The objectives of this research are to:

1. To synthesis the Fe/Zn-Zeolite-A catalyst.
2. To study the physicochemical properties of the modified catalyst.
3. To relate the physicochemical properties of the catalyst with the conversion of methane to the liquid hydrocarbons.

1.4 Scope of Research

The scopes of this study are divided into four stages:

- Preparation and modification of catalysts
- Characterization of the catalyst for its physicochemical properties
- Compare the physicochemical properties of modified zeolite with unmodified zeolite and previous research.
    - Predict the catalyst performance of methane conversion to liquid hydrocarbons based on the physicochemical properties of the catalyst.

CHAPTER 2

LITERATURE REVIEW

2.1 Methane Convert to Higher Hydrocarbon

The first step to convert methane to higher hydrocarbons is methane oxidation that will produce olefin. Higher hydrocarbons will be produced from reaction of olefin through oligomerization, dehydrocyclization and aromatization using zeolite base catalyst according to the reaction scheme below:

$$CH_4 + O_2(cat) \longrightarrow C_2H_6 \longrightarrow C_2H_4 \longrightarrow \text{Higher Hydrocarbons}$$

The combination of the oxidative catalysis of methane with acid catalyst in a single catalytic process over bifunctional oxidative acid catalyst would be possible to convert methane directly to liquid hydrocarbon. This could be done by modifying pentasil zeolite catalyst with a suitable element. One possibility of modifying zeolites is the replacement of some of the silicon and aluminum with transition metal (Mat *et al.,* 2006).

Numerous catalysts have been discovered which possess different activities and selectivities for methane conversion to higher hydrocarbon. Most of them are based on metal or transition metal oxides, which are often supported on silica and alumina.

Direct partial oxidation of methane with O_2 to higher liquid hydrocarbons over transition metal containing ZSM-5 catalyst is reported (Han *et al.,* 1994; Amin *et al.*, 2004). Han *et al.* (1994) found that the successful methane conversion to hydrocarbons can be done over metal-containing ZSM-5 catalyst to two effects:

i. Ability of the metal to show some limited activity to generate olefins from methane.
ii. Sufficient low olefin oxidation activity to allow the olefin produced to remain in the system.

Han *et al.* (1994), found that when Zn loaded into ZSM-5 beyond one wt% metal, it potentially to reduce desired catalyst acidity needed for the conversion of methanol produced to C_{5+}. During the early days, another synthetic zeolite (HZSM-5 Zeolite) was found to be a suitable catalyst for the conversion of the methane to higher hydrocarbons. The acidic HZSM-5 zeolite catalyst has shown a reasonable good aligomerization performance for olefin products to higher hydrocarbons.

2.2 Zeolites

By the conventional definition, zeolites are microporous aluminosilicates. This definition has been modified within the past years and nowadays isomorphously substituted materials, like for example gallosilicates, titanosilicates or aluminophosphates, are also called zeolites or zeolitic materials. Microporosity (pores with diameters below 2 nm) is an intrinsic feature of all these materials and is caused by channels and cavities within the crystal structures of zeolites (Baerlocher *et al.,* 2001).

The structure of zeolite as shown (Figure 2.1) consists the primary building units which cations coordinated tetrahedrally by oxygen. These tetrahedral are connected via corners, thus forming the crystal structure of the specific zeolite.

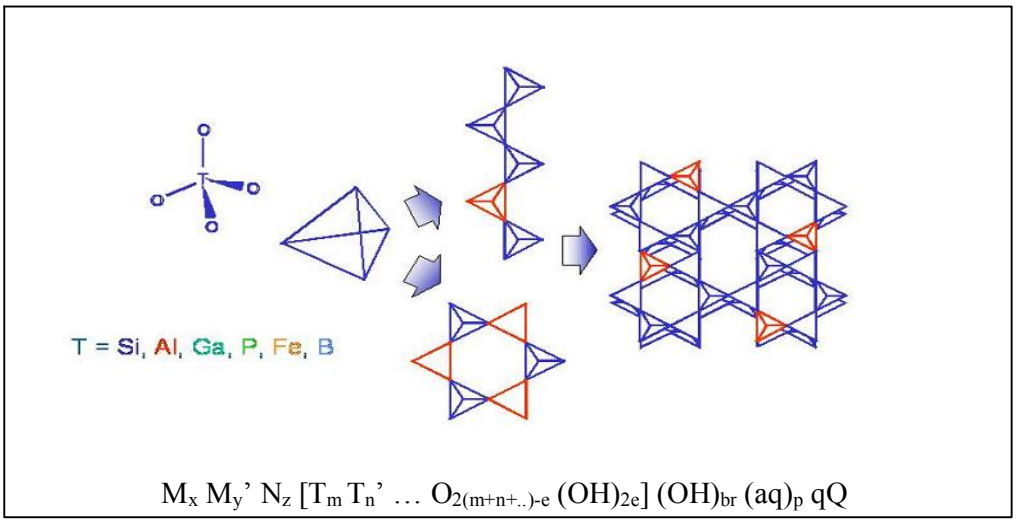

Figure 2.1 The Structure of Zeolite (Baerlocher *et al.,* 2001)

About 140 different zeolite structures are known of which about 40 are found in natural zeolites. The nomenclature of zeolites is rather confusing since every company is using its own names and abbreviations (Akporiaye *et al.,* 2001). To overcome this problem, a three-letter code system has been developed. These codes are assigned to specific structure type name *L*inde *T*ype A (Meier *et al.,* 1987). This structure type is found in various materials, as for example in aluminosilicates, aluminogermanates, gallophosphates or silicoaluminophosphates. A collection of all known zeolite structures can be found in the atlas of zeolite framework types or on the web page of the international zeolite association (Ch. Baerlocher *et al.,* 2001).

Zeolite-A exhibits the LTA (Linde Type A) structure and has a 3-dimensional pore structure with pores running perpendicular to each other in the x, y, and z planes, and is made of secondary building units 4, 6, 8, and 4-4. The pore diameter is defined by an eight member oxygen ring and is small at 4.2Å. This leads into a larger cavity of minimum free diameter 11.4Å. The cavity is surrounded by eight sodalite cages (truncated octahedra) connected by their square faces in a cubic structure.

The unit cell is cubic (a = 24.61Å) with Fm-3c symmetry. Zeolite-A has a void volume fraction of 0.47, with a Si/Al ratio of 1.0. It thermally decomposes at 700ºC. (Subhash Bhatia, 1990). Zeolite-A is of much interest because its supercage

structure is useful in spacio-specific catalysis. The inner cavity is large enough for structure changing reactions to take place, but the small pore means only a specific structure can get into the cavity for reaction, typically n-paraffins and olefins. One use is in paraffin cracking. The small entry pore is selective towards linear paraffins, and cracking can occur on sites within the supercage (alpha-cage) to produce smaller chain alkanes. Zeolite-A is also widely used in ion exchange separation (Ribeiro *et. al.,* 1984)

2.3 Zeolite Acidity

The concept that solid surfaces may be acidic arose from the observation that hydrocarbon reactions such as cracking that are catalyzed by acid treated clays or silica alumina, give rise to a much different product distribution than those obtained by thermal reaction (Knozinger *et al.,* 1997). These solid catalyzed reactions exhibit features similar to reaction catalyzed by mineral acids. By analogy to solution chemistry, it is postulated that the primary requirement for catalyst activity is that the solid be acidic and be capable of forming carbonium ions by reaction with a hydrocarbon (Subhash Bhatia *et al.,* 1990).

An acid site may be of the Bronsted type in which it denotes a proton to an unsaturated hydrocarbon, or of the Lewis type in which it acts as an electron acceptor, removing a hydride ion from a hydrocarbon (Pfeifer *et al.,* 1997). Acid catalysis is important in catalytic reforming, cracking, hydrocracking, isomerization, hydrodewaxing, alkylation and dealkylation (Farcasiu *et al.,* 1998). It is therefore important to be able to measure acidity and to rank solids as possible candidates for improvement of the yields of the processes.

The general definition of an acid is an electron-pair acceptor. The Bronsted acid site is able to transfer a proton from the solid to the absorbed molecule while the Lewis acid site is able to accept an electron pair from the adsorbed molecule and a coordinative bond with the surface is formed is shown in Figure 2.2.

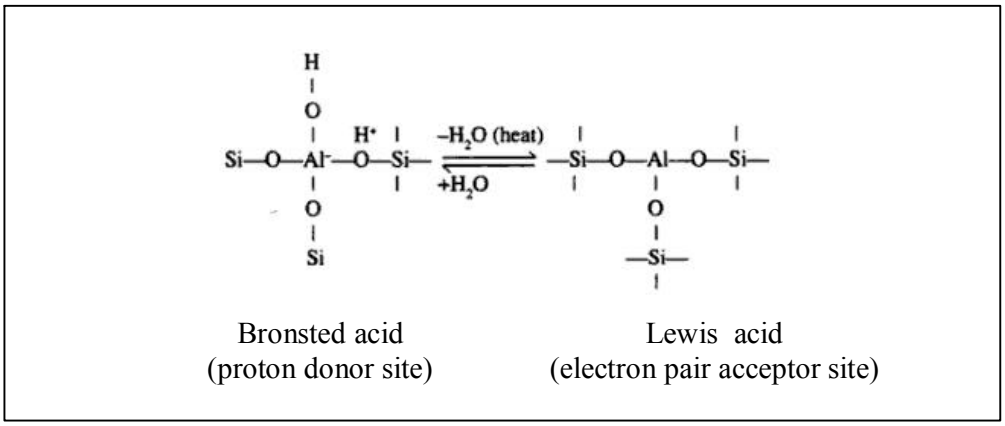

Figure 2.2 Acid Site (Subhash Bhatia *et. al.,* 1990)

A description of acidity in general and surface acidity more specifically, requires the determination of the nature, the strength, and the number of acid sites. A solid acid is capable of transforming an adsorbed basic molecule into its conjugated acid form (Artioli *et al.,* 2001).

The catalyst acidity indicated the total amount of acid sites of modified zeolite is higher than ZSM-5. The metal-loaded will increase the acidity of the catalyst and improve the conversion of the process (Amin *et.al.*, 2006).

2.4 Ga-HZSM-5

Gallium is one of the potential elements that could modify the properties of zeolites. Over this catalyst, higher quality gasoline yield was obtained in the oxidative methane conversion (Anggoro, D. D. *et al.,* 1998). Ga loaded on HZSM-5 is claimed to be very efficient for the aromatization of light alkenes and alkanes (Vermeiren *et al.,* 1989), and has the potential to convert methane to liquid hydrocarbons with high selectivity (Anggoro, D. D. *et al.,* 1998). HZSM-5 was modified with gallium by ion exchange to create a bifunctional catalyst with sites active in both acid catalysed and oxidation reactions for the conversion of methane to liquid hydrocarbons in a single catalytic step. The prepared catalyst, Ga-HZSM-5,

could act as a better bifunctional catalyst than its parent catalyst, HZSM-5 zeolite (Mat *et al.,* 1999).

2.5 W-HZSM-5

The W-HZSM-5 based catalyst was found to be a highly active catalyst for methane dehydroaromatization in the absence of oxygen (Zeng *et al., 2001*). The catalyst showed a high activity and a high heat resistivity under reaction temperature of 1073 K. It was also reported that the addition of a second metal component into the catalyst by sequence impregnation method such as Zn (or Mn, La, Mg, Li) on W/HZSM-5 (Xiong *et al.,* 2001) enhanced the catalytic performance. The work reported by Xiong *et al., (*2001) demonstrated that the catalyst with medium strength acidity could improve the dehydroaromatization of methane.

2.6 Zn-ZSM-5

In FT-IR study showed that zinc in the cationic position causes the generation of Lewis acid sites and decrease of the Bronsted. Disproportionation of toluene continuously decreases with increasing amount of Zn indicating the decline of the number of Bronsted acid site by introduction of zinc into zeolites. Aromatization of n-hexane on acid ZSM-5 zeolite is affected by the particle properties of the zeolite. The activity/selectivity of monofunctional acid catalysts is significantly higher on the HZSM-5 sample that has particles of smaller size, probably mainly due to the higher external surface of the zeolite (Agáta Smiešková *et al.,* 2004).

The selectivity of Zn-ZSM-5 catalysts continuously rises with increasing amount of Zn in the zeolite. This indicates the increase of the concentration of olefins precursors of aromatics in the reaction mixture due to the dehydrogenation activity of Zn species. Results showed that at higher Zn concentration the performance of Zn-

ZSM-5 catalysts is very different probably due to the fact that Zn species in the ZSM-5 zeolites in the case of higher Zn concentration are of different types (Agáta Smiešková *et al.,* 2004). The distances between the adjacent Al atoms in the zeolite framework affect the position of the zinc cations and determine if isolated or oxygen-bridged cationic species of Zn are created in the catalyst (A. Hagen *et al.,* 1994).

From the technological point of view it is important that the results call attention to the fact that besides of the composition and the acidity of the Zn-ZSM-5 catalysts, also the particle properties and aluminum distribution in the framework of the zeolite can affect the effectivity of Zn-ZSM-5 catalysts in aromatization of light alkanes (Agáta Smiešková *et al.,* 2004).

2.7 Mo-ZSM-5

Many progresses have been achieved since the first report on methane dehydro-aromatization over Mo/ZSM-5 in 1993 (L.Wang *et al.,* 1993). It is now generally accepted that the reaction takes place in two steps (Y.H. Kim *et al.,* 2000). In the early stages of the reaction, the molybdenum oxide is converted to MoC_x that later performs the CH_4 dehydrogenation and coupling to ethylene. Then, in a second step, the ethylene is oligomerized to benzene on the Brønsted acid sites of the zeolite (Figure 2.3). The location of the molybdenum plays a major role in this general scheme.

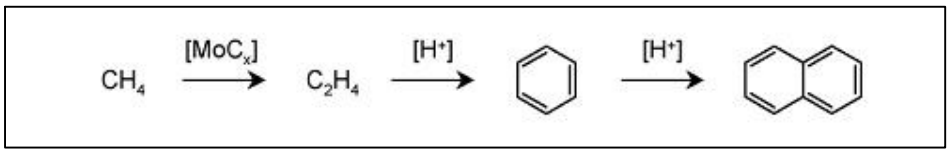

Figure 2.3 Formation of benzene and naphthalene from methane on Mo/ZSM-5 (Jean-Philippe Tessonnier *et al.,* 2007)

Molybdenum oxide supported on classical supports like SiO_2, Al_2O_3 or TiO_2 is quickly carburized to MoC_2 under the reaction conditions and then only catalyses